Hot Hydrogen Testing of W-coated dUN Kernels for Nuclear Thermal Propulsion

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Tungsten-coated kernels of uranium nitride (UN) are a possible reactor fuel component for nuclear thermal propulsion. Hot hydrogen testing of such kernels (approx. 250µm diameter, coating thickness 5µm) has been performed at temperatures from 1800°C to 2300°C for 30min each, using depleted uranium nitride (dUN). In addition to direct observations and mass loss measurements, the samples were analyzed by XRD and SEM/EDS after each run. Decomposition of dUN and the formation of molten uranium happened at all temperatures tested with reaction rates increasing with temperature, despite the tungsten coating. At 2300°C, the kernels disintegrated and molten uranium seeped through the wall and bottom of the tungsten crucible employed. These hot hydrogen tests allowed to test the integrity of the tungsten coating and addressed the operating limits of the loose tungsten-coated dUN kernels. Improved results are expected upon consolidation of the tungsten-coated dUN kernels in a Mo-W alloy matrix.

I. INTRODUCTION

For space nuclear propulsion (SNP), specifically nuclear thermal propulsion (NTP), a number of uranium-bearing materials and composites have been discussed as reactor fuels. Due to the required temperatures of the hydrogen propellant at or near 3000K, the reactor fuel and any supporting materials in contact with it have to withstand those temperatures, in a hydrogen atmosphere. Examples of nuclear fuels being considered are UC, UN, UO_2 (Ref. 1). Uranium mononitride (UN) is advantageous with respect to uranium concentration and thermal neutron absorption cross section. It is, however, known and well documented in the literature that UN already dissociates into U and N_2 at temperatures at or above 1800°C (Refs. 2-5), with some sources showing some dissociation already at 1600°C (Ref. 5). A nitrogen counterpressure of at least 2.5bar (Ref. 2) can suppress or reduce the dissociation. Thus, the addition of such a counterpressure system is highly recommended for future reactor designs employing UN fuel. Embedding the ceramic fuel material in a metallic ("cermet") or ceramic ("cercer") matrix that can withstand those temperatures might also suppress or reduce the dissociation by keeping the initially released nitrogen from escaping and providing the necessary counterpressure internally on a microscopic level. A first step towards such a matrix is a coating of the kernels with the respective metal or ceramic. In this work, spherical UN kernels using depleted uranium (dUN), coated with tungsten, have been evaluated under hot hydrogen testing for temperatures from 1800°C to 2300°C (2073-2573K).

II. EXPERIMENTAL

II.A. Sample Composition

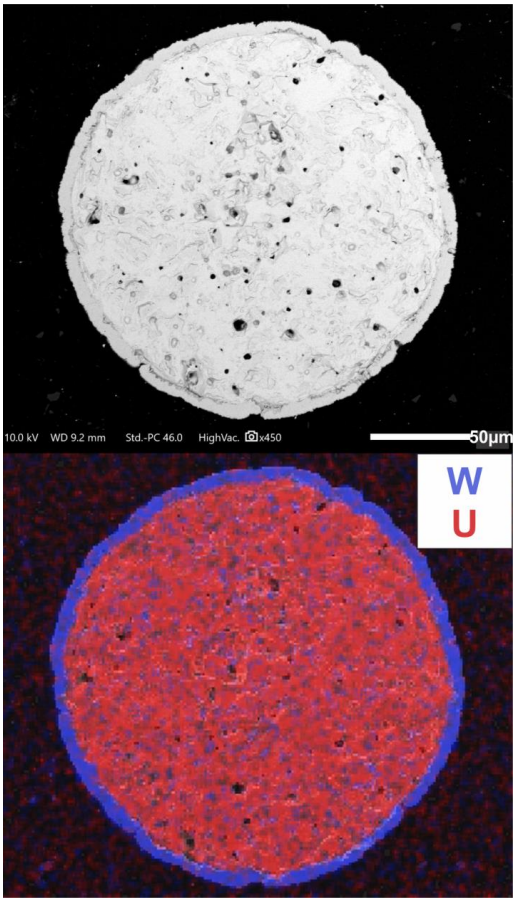

Fig. 1. SEM image (BSE) and EDS scan of the cross section of a spherical W-coated dUN kernel.

The samples consisted of spherical dUN kernels of 220 - 280µm diameter, with a tungsten coating of approximately 5µm thickness. A cross section of an unprocessed kernel can be seen in figure 1. The development of the PVD coating process and the production of the kernels was done by BWX Technologies (BWXT) in Lynchburg, VA, as part of the SNP Fuel and Moderator Development Program (FMDP). The batch no. of the kernels used was BW-511696-W. For each of the hot hydrogen runs, about 2.1-2.2 g of unprocessed material were used (compare table 1). Before and after each run, the combined sample and crucible were weighed to determine the mass loss rate.

II.B. Hot Hydrogen Testing

The hot hydrogen tests were performed in the "Compact Fuel Element Environmental Test" (CFEET) facility at NASA Marshall Space Flight Center. It consists of a hermetically sealed chamber with an internal induction coil for heating and an inlet for the processing gas (processing under vacuum is also possible). More information on CFEET can be found in refs. 6, 7. A tungsten susceptor surrounding the sample is usually employed for heating and for directing the hydrogen gas flow. Before processing, the chamber is evacuated to about $2.5 \cdot 10^{-2}$ mbar, flushed with high purity argon, and evacuated again, before the final filling with hydrogen. Process gas pressures are at or slightly above ambient pressure. The hydrogen (Ultra High Purity H_2) flow rate employed for these tests was 13.8 SLPM. The coated UN kernels were held in a 3D-printed tungsten crucible of 12mm OD and 8mm ID. Figure 2 shows the crucible and the tungsten pieces holding it in the coil center plus the tungsten susceptor. The crucible was heat treated and carburized using carbon black on the inside at 2370°C for 30 min before processing, to reduce sticking with the W-coated kernels. Filling the crucible with acetone as liquid showed no leakage of fluid.

The maximum achievable temperature in this setup depends somewhat on the sample as well as gas type and flow rate – for the W-coated dUN kernels in the crucible, this was 2300°C. The sample temperature was measured through a fused quartz window directly on the kernel surface with a multi-wavelength spectropyrometer (FAR FMP2/2X, 1073-4273 K). After an initial preheating stage at 1430°C for 5 minutes to reduce heat-up time to the final temperature, four different temperatures were employed for 30 min each, 1800°C, 2000°C, 2200°C, and 2300°C. After the 30 min processing time, power was shut off and the samples cooled down rapidly in flowing hydrogen (for 15 min) and argon (10min), followed by a final 1h passive cooldown in argon before extraction.

Fig. 2. 3D-printed tungsten crucible (upper left) to hold the sample kernels on top of the tungsten "pedestal," and the other tungsten pieces below that shape the gas flow. The tungsten susceptor (1" ID) shown on the right sits on the rim of the part below the pedestal during processing, surrounding the sample.

II.C. Sample Analysis Methods

II.A.1. X-Ray Powder Diffraction

XRD data (Instrument: Aeris Research Edition from Malvern Panalytical, Cu-K_α radiation) were taken from each sample after processing, as well as from the unprocessed material, to track phase changes with processing temperature. The 2θ range employed was 5°-142.5°, with a scan step size of 0.011° and an integrated scan step time of 599s. The kernels were held in the well of a silicon zero diffraction plate under Kapton® tape. Phase analysis was done using the HighScore+ software by Malvern Panalytical together with the ICDD PDF-4+ 2020 database.

II.A.1. SEM and EDS Analysis

SEM images of the samples and EDS data of their elemental composition were obtained by a JEOL JSM-IT200 instrument.

III. RESULTS AND DISCUSSION

III.A. General

III.A.1. Visual Inspection

The visual appearance for the different processing temperatures and other observations are listed in table I below. Up to 2200°C, the kernels appeared visually unchanged to the unaided eye, although the fact that the window and walls above the sample were radioactive after each run already at 1800°C, points to some uranium loss.

TABLE I. Sample appearances and general observations for each process temperature. Process time was 30min for each of the runs.

Sample temperature	Visual inspection	Remarks
Unprocessed	Grey loose kernels	-
1800°C	Visually unchanged	Chamber window and walls slightly radioactive after processing.
2000°C	Visually unchanged; some kernels stick to the wall	
2200°C		
2300°C	Liquid uranium seeped through crucible walls and bottom (figure 3); remaining kernel parts changed color to brown	Chamber window fogged and window and walls are radioactive.

A significant change happened at 2300°C – during the 30min of processing, the sample temperature dropped slowly from 2300°C to about 2220°C at full power. When the crucible was finally retrieved after cooldown, it became apparent that liquid uranium had seeped through the walls and bottom of the crucible and bonded it to the pedestal as shown in figure 3, which lead to enhanced thermal conduction through the pedestal to the cold side of the setup, resulting in the observed temperature drop.

III.A.2. Mass Loss Data

The mass loss data for each run from 1800°C to 2200°C are listed in table II. One can see a slight increase with increasing temperature. It should be noted that those numbers are similar to mass loss data noted by Baranov et al.[5] for uncoated uranium nitride at 1900°C. They reported mass loss rates of 0.017-0.019%/min, equivalent to 0.51-0.57% in 30min. Again, the fact that the window and upper walls of the furnace were radioactive after each run shows that uranium loss was part of the mass loss in each case. No mass loss rate could obviously be measured for the 2300 °C run, due to the liquid uranium seeping out of the crucible.

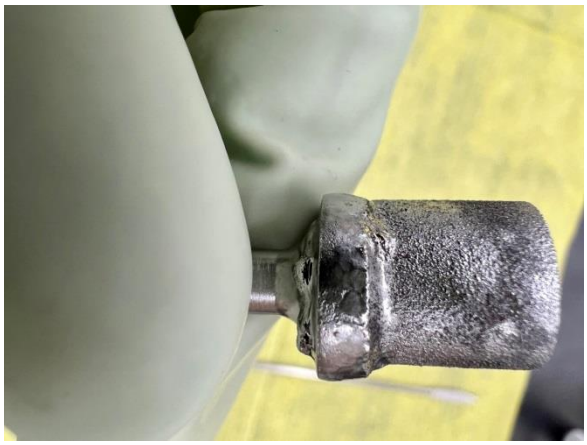

Fig. 3. Tungsten crucible bonded to the pedestal and partially coated by liquid uranium seeping out from the inside after processing the W-coated dUN kernels for 30min at 2300°C. The crucible OD was 12mm.

TABLE II. Mass loss data for each process temperature

Sample temperature	Sample Mass [g]	Mass loss [mg]	Mass loss [%]
1800°C	2.13128	14.5	0.68
2000°C	2.12834	15.0	0.70
2200°C	2.18600	22.7	1.04
2300°C	2.13400	n/a (see text and Table I)	

III.B. X-Ray Diffraction

The XRD results are shown in figure 4 and summarized in table III. The unprocessed kernels only show the peaks for tungsten, but after the 1800°C hot hydrogen treatment, traces of dUN and the high-temperature cubic phase of metallic uranium, γ-U, could be found, although at small concentrations (the peak heights were less than 1% compared to the 100% peak from tungsten). At 2000°C, the peaks get higher, but are still below 1%. Possible traces of a hexagonal tungsten nitride phase ("δ_H^{IV}" = $WN_{0.91}$ and/or $WN_{1.67}$, Ref. 11) can be detected at 2000°C and 2200°C. At 2200°C and 2300°C, the additional peaks are clearly visible (figure 4) and at 2300°C the highest peak is no longer a tungsten one, but a joint one of dUN and γ-U. In addition to dUN, γ-U, and possible traces of tungsten nitrides, strong lines of uranium hydride, β-UH_3, are found in the 2300°C and 2200°C samples. β-UH_3, which has a brown color (compare 2300°C entry in table I), typically forms at 250°C to 320°C from uranium metal and hydrogen, and decomposes around 500°C (Ref. 8). It can therefore be

safely assumed that it formed during cooldown of the sample.

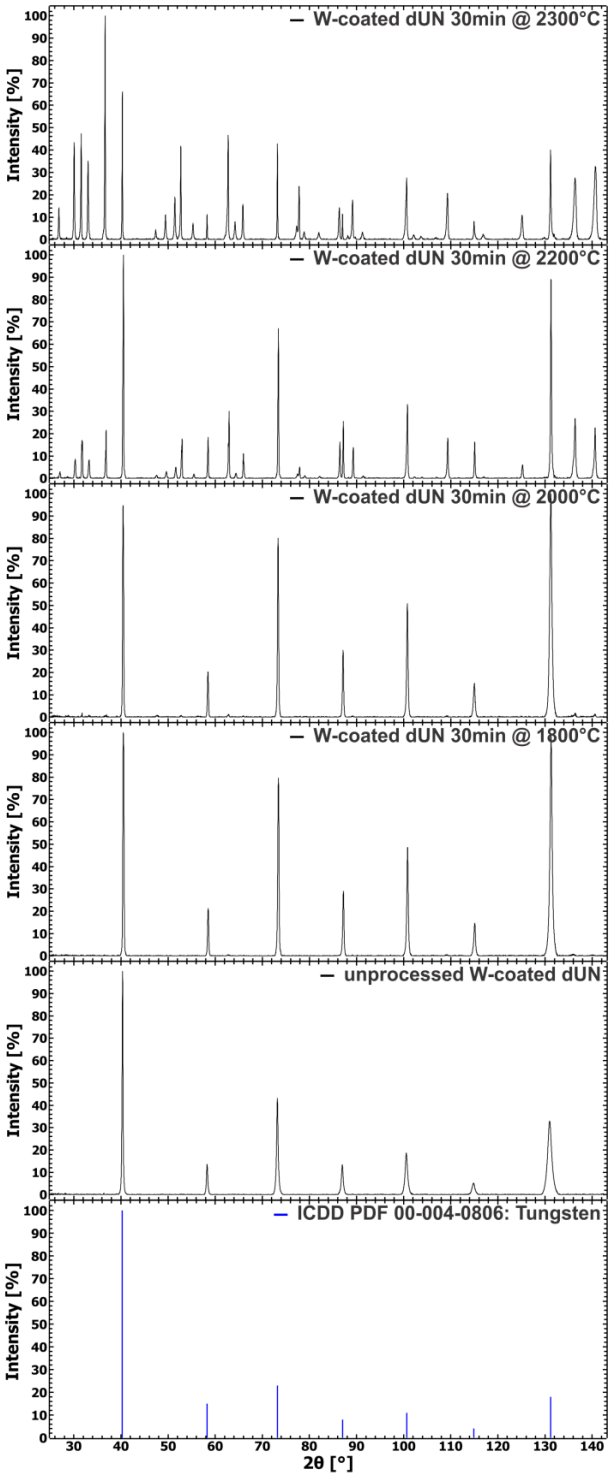

Fig. 4. XRD spectra for Cu-$K_{\alpha 1}$ radiation of the samples plus an ICDD PDF-4+ 2020 reference of tungsten for comparison (bottom graph). The 2θ range shown is 25-143°.

TABLE III. Phases according to the XRD analysis

Sample	Phases
unprocessed	W
1800 °C	W, traces of dUN and γ-U
2000 °C	W, traces of dUN, γ-U, traces of δ_H^{IV-} tungsten nitride[11]
2200 °C	W, dUN, γ-U, β-UH_3, traces of δ_H^{IV-} tungsten nitride[11]
2300 °C	W, dUN, γ-U, β-UH_3

III.C. SEM and EDS analysis

SEM images of the kernels before and after processing, plus corresponding EDS maps for tungsten and uranium, are shown in figures 5-9. The unprocessed kernels show essentially a tungsten surface, with the exception of a few broken ones showing the dUN interior (figure 5).

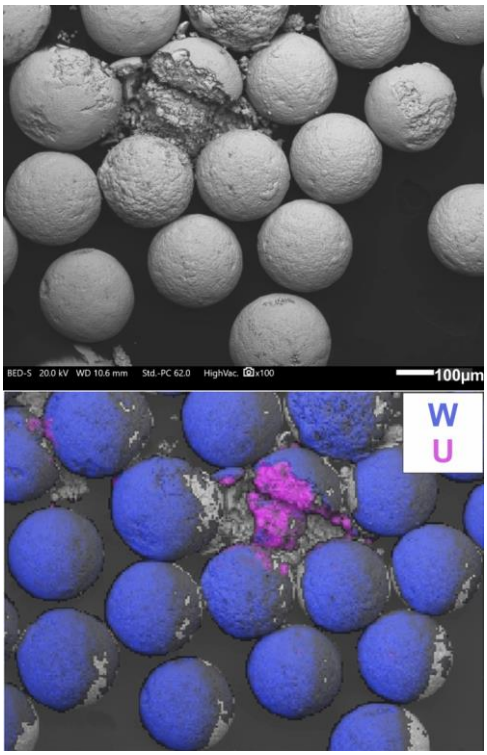

Fig. 5. SEM image and EDS color-coded map of the unprocessed W-coated dUN-kernels. A few kernels were broken and revealed the dUN as can be seen in the EDS, but otherwise no uranium can be detected on the kernel surface.

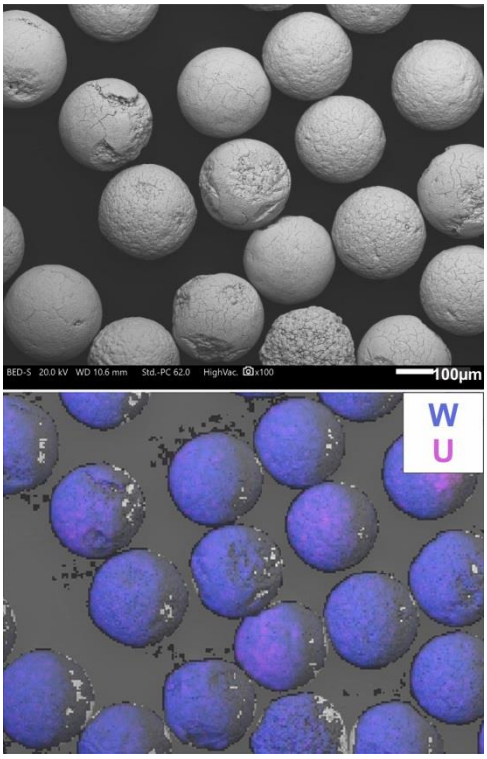

Fig. 6. SEM image and EDS color-coded map of the kernels after the 1800°C test. Small cracks can be seen in the surface of some kernels (top image) and nearly all kernel surfaces show traces of uranium contamination, as opposed to the unprocessed kernels (figure 5).

At 1800°C, the kernels exhibit some fine cracking on the surface and nearly all of them show traces of uranium on the outside (figure 6). There is a possibility that the uranium on the outside was deposited from previously broken kernels, but uranium seeping through the cracks or grain boundaries from the inside is more likely (compare section IV.).

At 2000°C, however, the picture is clear: significantly more uranium is seen on the surface (figure 7, top part), shown to be areas of molten metal on the surface coming out of cracks or grain boundaries, as seen in the higher magnification of the lower two images of figure 7. The EDS image shows uranium and not tungsten in those areas. This process is further increased at 2200°C with some kernels already cracking and breaking up (figure 8, top two images) and expanded areas of uranium metal on the surface of intact kernels (figure 8, bottom images).

The 2300°C sample (figure 9) shows disintegration of all kernels, with a mix of uranium and tungsten in the elemental analysis of the fragments.

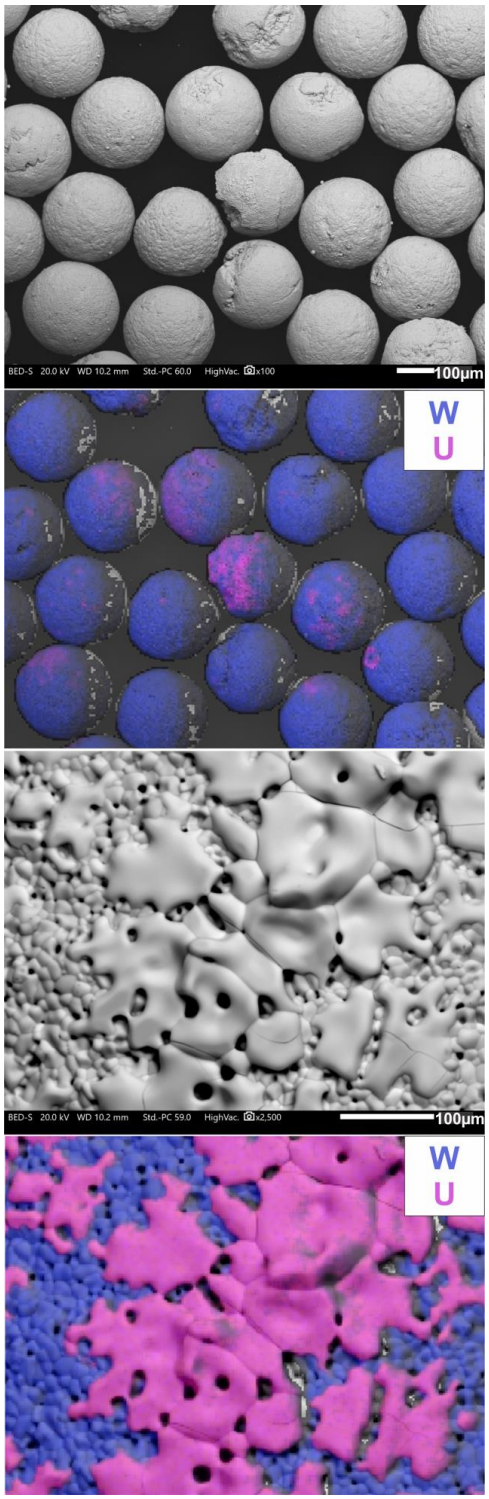

Fig. 7. SEM images and EDS color-coded maps of the kernels at 2 different magnifications after the 2000°C test. Uranium is present on all surfaces. The enlarged view shows that these areas are associated with grain boundaries or cracks of the tungsten and consist of molten uranium.

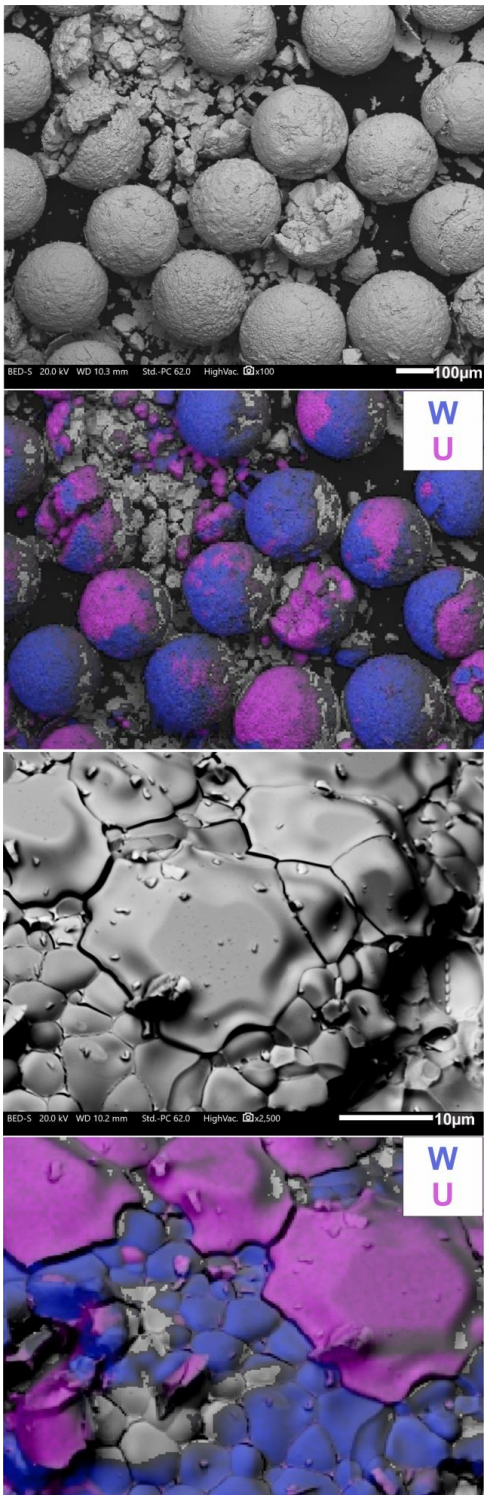

Fig. 8. SEM images and EDS color-coded maps of the kernels at 2 different magnifications after the 2200°C test. Melt covers even larger areas of the kernel surface and some kernels are fragmenting. The enlarged view shows that these are areas associated with grain boundaries or cracks of the tungsten and consist of molten uranium.

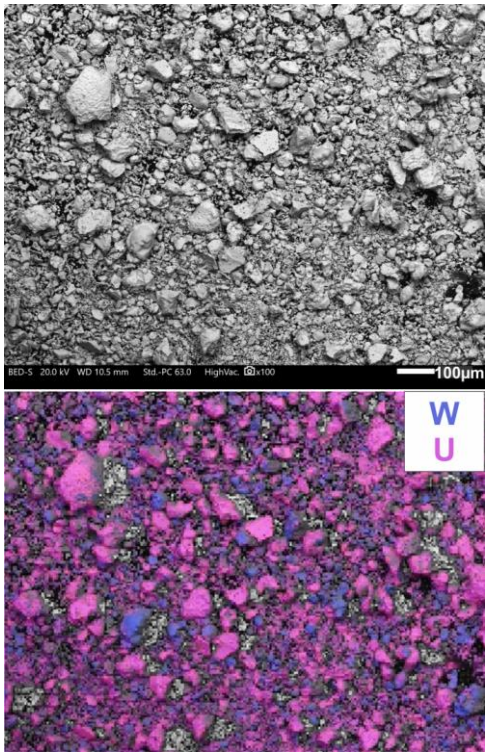

Fig. 9. SEM image and EDS color-coded map of the kernels after the 2300°C test. No intact kernels remain, only small fragments can be seen. The elemental map shows a random mix of uranium and tungsten.

IV. DISCUSSION AND CONCLUSIONS

The direct observations, mass loss data, XRD analysis, and SEM/EDS analysis of the samples subjected to hot hydrogen processing all point in the same direction: processing at these temperatures leads to some dissociation of dUN and the resulting formation of (molten) uranium metal, despite the tungsten coating. This was proven by the mass loss measurements, the results of the XRD measurements showing free uranium and UH_3 (formed from uranium metal and H_2 during cooldown of the sample), as well as the results of the SEM and EDS analysis of the kernels. The molten uranium is able to seep through the tungsten coating, and larger amounts can even seep through the walls of the tungsten crucible, as shown in the 2300°C run (figure 3).

A similar destructive effect of uranium on tungsten crucibles, also at 2300°C, was reported by Baranov et al.[5] – their DTG crucible made from tungsten was essentially destroyed by the uranium at this temperature. The mechanism for this has been investigated in the 1980's by Kuznietz et al.[9]: Although tungsten, unlike molybdenum[10], cannot be dissolved by molten uranium, the uranium readily infiltrates the grain boundaries and releases the grains in a liquid embrittlement process.

According to the results of Kuznietz et al.[9], complete infiltration of the grain boundaries happens already at and above 1255°C, well below the temperatures employed here. Due to this effect, no buildup of internal nitrogen pressure to reduce further dissociation of dUN after the initial one appears sustainable. A possible formation of tungsten nitrides at intermediate temperatures of 2000°C-2200°C as indicated by the XRD results would also reduce temporarily any internal N_2 pressure buildup.

Future hot hydrogen tests are planned for samples where these kernels are consolidated in a Mo-W alloy matrix using spark plasma sintering (SPS), to hopefully decrease the dUN dissociation in a more massive metallic environment.

ACKNOWLEDGEMENTS

This work was completed at NASA - Marshall Space Flight Center and supported by NASA's Space Technology Mission Directorate (STMD) through the Space Nuclear Propulsion (SNP) project. The University of Alabama in Huntsville part of the research was supported by NASA under cooperative agreement NNM11AA01A. The fabrication of the dUN fuel kernels was completed by BWX Technologies, Inc. under BEA contract no. 00212687. The manufacturing of the tungsten crucibles by Omar R. Mireles from NASA-MSFC is greatly appreciated.

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